“Development of Carbon based Composite Gas Sensors”

A Synopsis Submitted

To

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By

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SYNOPSIS

Abstract of proposed work plan/ problem:

1. Introduction

With the development of urbanization and industrialization, people's lifestyles have been changed dramatically over the past several decades. Unfortunately, air pollutions caused by toxic gas emissions from constructions, indoor decorations, household equipment and the outside atmosphere have become a global issue because of the serious threat to human health and life.It is due to increased consciousness about potential environmental hazards, environmental gas monitoring has become an important research area. Therefore, it is of urgent need to fabricate new sensing materials with a high sensitivity and efficiency for indoor volatile organic compounds[1-2].

Most of the common commercial gas sensors are based on metal oxide semiconductors, polymer materials and the methods used for sensing are optical methods, calorimetric methods, gas chromatography, and acoustic methods. The limitations of these gas sensors can be one or more of the following: costly, sensitivity in ppb level is rare, selectivity is poor, life time is limited, repeatability is poor, miniaturization is difficult, power consumption is high[3]. As an alternative, nano-material based gas-sensing materials have gained significant momentum due to many promising electrical, optical, and thermal properties combined with, high surface to volume ratio, short response and recovery times, high sensitivity, selectivity, reversibility and stability etc. Different carbon materials, such as carbon nanotubes (CNT), charcoal, graphene, grapheme oxide (GO), bio char, etc. have been shown to be useful as chemical and bio-sensors due to the ease in tailoring their sensitivity by simple chemical treatments[4].

On the other hand, carbon based materials having a great number of desirable features such as low cost, availability, high surface area, unique pore structure and act as active nanocomposites showing high gas sensing behaviors, catalyst and adsorbents for the removal of organic pollutants at room temperature. Functionalization of carbon-based materials can modify their surface, interfacial, and electronic properties, thereby further increasing their utility across a wide range of applications. Even though these carbons based materials have lack of selectivity. This limitation can be overcome through their chemical modification and/or their doping with metal/metal oxides or any inorganic material.[5].Hence, the main aim of the proposed work is to develop nanocomposites for sensor application

2.Review of literature and development in the subject(previous work done in the relevant area)

The exceptional electronic and mechanical properties and the solution dispersibility of fullerenes and carbon nanotubes (CNTs) have drawn considerable attention to these carbon allotropes for nearly three decades [6-7]. Zero-dimensional (0D) buckminsterfullerene, discovered by Kroto, Curl, and Smalleyin1985 [8].ignited significant interest in nano scale carbonaceous materials. 1D CNTs, highlighted shortly thereafter by Iijima [9]. Further increased enthusiasm in

carbon-based nanoparticle research. While both fullerenes and CNTs are proposed to have been derived from the 2D graphene sheet, only since its recent isolation in 2004 has this parent carbon monolayer found its place in the limelight[10–13].Numbers of groups are working on nanocomposites for sensor application. The details are as follows.

National status

R.S.Khairnaret.al. in 2014 have used minute amount of CNT in nano-HAp which increases the porosity of nano-HAp significantly while offering large effective surface area to sensor matrix. It is observed that the operating temperature of pure HAp for sensing CO2 gas is 1600C while the CNT blended nano-HAp can sense CO2 gas at temperature as low as 700C. Thus 0.1wt% CNT doped nano-HAp is found to be promising gas sensing material for practical CO2 gas sensor. It has fast response to CO2 gas while exhibiting better recovery at low operating temperature.[14]

Nanocomposite of graphene/ZnO was prepared through situ reduction method during refluxing by Kanika Anand et al in 2014. It was concluded that the existence of graphene in the composites facilitated the electrontransfer and electrical conductivity. The composite sensors have showed improved performance at a lower temperature relative to that of the corresponding bare ZnO [15]. Abdulla et al has studied the highly sensitive, room temperature gas sensor based on polyaniline-multiwalled carbon nanotubes (PANI/MWCNTs) nanocomposite for trace-level ammonia detection [16]. Anand, Kanika et al has studied the hydrogen sensor based on graphene/ZnO-nanocomposite [17]. Kar, Pradip et al has studied the carboxylic acid functionalized multi-walled carbon nanotube doped polyaniline for chloroform sensors [18].

Tyagi, Punit et al has studied the a comparative study of RGO-SnO2 and MWCNT-SnO2 nanocomposites based SO2 gas sensors.[19]. Serban, Bogdan et al has studied Polymer-amino carbon nanotube nanocomposites for surface acoustic wave CO2 detection.[20].Kumar et.al.has studied the poly (lactic acid)–multi-wall carbon nanotube conductive biopolymer nanocomposite vapour sensors [21]. Srivastava, Shubhda, et al has studied, the faster response of NO2 sensing in graphene–WO3 nanocomposites [22]. Kaur, Jasmeet, et al has studied sensitive and selective acetone sensor based on Gd doped WO3/reduced graphene oxide nanocomposite [23]. Veeramani et al it has studied heteroatom-enriched porous carbon/nickel oxide nanocomposites as enzyme-free highly sensitive sensors for detection of glucose [24].

International status:

Zilli, D et al has studied room temperature hydrogen gas sensor nanocomposite based on Pd-decorated multi-walled carbon nanotubes thin films [25]. Sayago, I.et al has studied the new sensitive layers for surface acoustic wave gas sensors based on polymer and carbon nanotube composites[26].Van Hieu et al has studied the thin film polypyrrole/SWCNTs nanocomposites based NH3 sensor operated at room temperature [27]. Serban et al has studied matrix nanocomposite containing aminocarbon nanotubes for carbon dioxide sensor detection [28]. Liu

et al has studied direct electrodeposition of graphene enabling the one-step synthesis of graphene-metal nanocomposite films [29]. Zarrin et al has studied the functionalized graphene oxide nanocomposite membrane for low humidity and high temperature proton exchange membrane fuel cells [30]. Wang, Yizhong et al it has studied passive wireless surface acoustic wave CO2 sensor with carbon nanotube nanocomposite as an interface layer [31]. Baibarac et al has studied nanocomposites based on conducting polymers and carbon nanotubes, from fancy materials to functional applications [32]. Mun et al has studied the cellulose-titanium-multiwalled carbon nanotube hybrid nanocomposite and its ammonia gas sensing properties at room temperature [33]. Aroutiounian et al has studied the surface-ruthenated SnO2/MWCNTs nanocomposite thick-film gas sensor [34].

Objectives of the research

Researchers have used carbon composites in the form of films. But now-a-days nanocomposites have attracted the researchers because of their special properties. Nanocomposites can improve any property of the substance like increase in the gas sensing property. There are very few reports related in sensor application. Hence, main aim of our research work is to develop carbon based nanocomposites for sensor application.

The objectives of the research work are as follows,

1. To prepare carbon based nanocomposite materials.
2. To characterize nanocomposites by techniques like XRD, FTIR, SEM/EDS, AFM, TG/DTA, etc.
3. Utilization of nanocomposites as gas sensors for various gases and optimization of various sensor parameters.

3. Methodology

So first we have to synthesize/procure carbon based material. Carbon based material will be characterized by different techniques like XRD, FTIR, SEM/EDS, AFM, TG/DTA, etc. Then for the formation of nanocomposites we have to search for a good filler or reinforcing material. This filler/reinforcing material is characterized by various characterization techniques.

Different proportions of filler/reinforcing material and main substrate give different results for the gas sensing purposes. So different proportions of the filler and substrate material may be used to get the best possible results. So selection of a suitable filler/reinforcing material is an important step in the formation of nanocomposites for the gas sensing application. These nanocomposites formed are also characterized by various characterization techniques. Finally we will test these studies and optimize for the various gas sensor parameters.

The two probe electrical experimental set up will be design and fabricated as per the requirement of the sensor substrate the experimental set up will be consist of stainless steel electrical heater, copper electrode, thermocouple for temperature measurement and other measurement units like current meter and voltmeter. The provisional will be made to introduce the vapours / gas molecules in the vicinity of substrate with the concentration as low as 10 ppm. This material will be converted in the form of thick film substrate by means of screen printing

technique. The screen printing will be developed and standard for making thick film with varying thickness in the range of 10 to 1000 micron. The substrate for thick film deposition will be either glass or alumina ceramic material. This thick film use for gas sensing. The characterization will be carried out of this thick film by means of XRD, AFM, SEM, TGA-DTA and FTIR. Operating temperature for gas sensor will be evaluated for various gas concentrations as well as at various temperatures. Gas response-recovery time and saturation will be studied from point view of utilizing these systems for gas sensing devices.

4. Importance of study / society applications

We know that our environment is polluted by different poisonous gases. Various gas sensors have been developed by the researchers for the gas sensing application. It is better for us to detect these harmful gases at its lowest possible gases so as to reduce its effects on environment. So there is always a scope of a good gas sensor .A good gas sensor is one which can detect these poisonous or hazardous gases at its lowest concentration and can operate at the lower operating temperature (possibly up to room temperature). So our present study will be focused on trying to minimise the operating temperature of the sensor and to enhance its gas sensing property.

Significance of the study

The present research work in the area of sensors is being further extended in the development of different kind of Gas sensors using Carbon based nanocomposites. The study, in particular, will be useful in sensing the gases and vapours when they are present in meagre amounts. For example, the ammonia, Ethanol, Methanol sensing with Carbon based nanocomposites will be useful in detecting bombs located in strategic areas, drunk drivers cars controlled. Similarly, the detection of carbon containing gas vapour will be useful in monitoring environment. The results obtained by carrying out this research work is also beneficial to industrial processing, specially in chemical industries and drug formulation processing.

5. Proposed work plan/ formulation and structure of study

It is proposed to make an intensive literature survey in the gas sensors pertaining to Carbon based nanocomposites. The Carbon based nanocomposites will be taken up as a base substrate (sensor bed) for sensing various gases and vapours. These sensor beds will be investigated for their sensing behaviour for various gases/vapours as a function of gas concentrations and also as a function of sensor bed temperature. The sensor material will be characterized by AFM, SEM and XRD for their surface topography at nanoscale, at microscale and structural determination respectively. The two probe set up will be used specially for carrying out the resistivity measurement. This will provide the gas sensitivity as a function of temperature. Similar experiments will be carried out for different ppm concentrations of gases/vapours. The response and recovery characteristics will be investigated to see its practical and commercial use as a sensor device. The developed sensors systems will be compared with the existing sensors in the market.

Year wise plan

The following work will be carried out as per the time duration listed below.

First Year: Completion of Pre-Ph.D. guide's course, literature Survey, understanding of experimental setup, to gain expertise in handling sophisticated instruments like XRD,FTIR, SEM/EDS, TG/DTA. Development of screen printing setup and its standardization, participation in Symposium/seminars/conferences/workshops.

Second Year: Synthesis of Samples, characterization of Synthesized samples by XRD, FTIR, SEM/EDS,AFM,TG/DTA, etc. for physical and Chemical investigations, composite preparation, preliminary study on sensor behavior, participation and presentation in International and national seminars/conferences/workshops/symposium.

Third Year: Investigation of gas sensing behavior of carbon based nanocomposites thick films gas sensors. Paper publications, Thesis writing and submission.

6.References

[1] Liu, Y., Chen, J., Li, W.,Shen, D., Zhao, Y., Pal, M., Zhao, D. (2016). Carbon functionalized mesoporous silica-based gas sensors for indoor volatile organic compounds. Journal of Colloid and Interface Science, 477, 54–63. doi:10.1016/j.jcis.2016.05.040

[2] Mahabole, M. P., Lakhane, M. A., Choudhari, A. L., &Khairnar, R. S. (2016). Development of metal oxide impregnated stilbite thick film ethanol sensor. doi:10.1063/1.4946349

[3] Gupta Chatterjee, S., Chatterjee, S., Ray, A. K., &Chakraborty, A. K. (2015). Graphene–metal oxide nanohybrids for toxic gas sensor: A review. Sensors and Actuators B: Chemical, 221, 1170–1181. doi:10.1016/j.snb.2015.07.070

[4]X. Liu, S. Chang, H. Liu, S. Hu, D. Zhang, H. Ning, A survey on gas sensingtechnology, Sensors 12 (2012) 9635–9665.

[5]Al-Enizi, A. M., Naushad, M., Al-Muhtaseb, A. H., Ruksana, Alshehri, S. M., Alothman, Z. A., &Ahamad, T. (2018). Synthesis and characterization of highly selective and sensitive Sn/SnO 2 /N-doped carbon nanocomposite (Sn/SnO 2 @NGC) for sensing toxic NH 3 gas. Chemical Engineering Journal, 345, 58–66. doi:10.1016/j.cej.2018.03.138

[6] A. K. Geim, K. S. Novoselov,Nat. Mater.2007,6, 183–191.

[7] P. Avouris, Z. H. Chen, V. Perebeinos,Nat. Nanotechnol.2007,2,605–615.

[8] H. W. Kroto, J. R. Heath, S. C. Obrien, R. F. Curl, R. E. Smalley,Nature1985,318, 162–163.

[9] S. Iijima,Nature1991,354, 56–58.

[10] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas,A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff,Carbon2007,45, 1558–1565.

[11] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich,S. V. Morozov, A. K. Geim,Proc. Natl. Acad. Sci. USA2005,102,10451–10453.

[12] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang,S. V. Dubonos, I. V. Grigorieva, A. A. Firsov,Science2004,306,666–669

[13] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li,J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, W. A. de Heer,Science2006,312, 1191–1196

[14] R. S. Khairnar, S. R. Anjum, M. P. Mahabole . Development of CNT doped nano-HAp thick film gas sensor. International Journal of Engineering Science and Innovative Technology (IJESIT) Volume 3, Issue 3, May 2014

[15]Anand, K., Singh, O., Singh, M. P., Kaur, J., & Singh, R. C. (2014). *Hydrogen sensor based on graphene/ZnOnanocomposite. Sensors and Actuators B: Chemical, 195, 409–415.* doi:10.1016/j.snb.2014.01.029

[16] Abdulla, Sukhananazerin, Thalakkotur Lazar Mathew, and BijiPullithadathil. "Highly sensitive, room temperature gas sensor based on polyaniline-multiwalled carbon nanotubes (PANI/MWCNTs) nanocomposite for trace-level ammonia detection." *Sensors and Actuators B: Chemical* 221 (2015): 1523-1534.

[17]Anand, Kanika, et al. "Hydrogen sensor based on graphene/ZnOnanocomposite." *Sensors and Actuators B: Chemical* 195 (2014): 409-415.

[18]Kar, Pradip, and Arup Choudhury. "Carboxylic acid functionalized multi-walled carbon nanotube doped polyaniline for chloroform sensors." *Sensors and actuators B: Chemical* 183 (2013): 25-33.

[19]Tyagi, Punit, et al. "A comparative study of RGO-SnO2 and MWCNT-SnO2 nanocomposites based SO2 gas sensors." *Sensors and Actuators B: Chemical* 248 (2017): 980-986.

[20]Serban, Bogdan, et al. "Polymer-amino carbon nanotube nanocomposites for surface acoustic wave CO2 detection." *Romanian Journal of Information science and technology* 12.3 (2009): 376-384.

[21]Kumar, Bijandra, Mickaël Castro, and Jean-François Feller. "Poly (lactic acid)–multi-wall carbon nanotube conductive biopolymer nanocompositevapour sensors." *Sensors and Actuators B: Chemical* 161.1 (2012): 621-628.

[22]Srivastava, Shubhda, et al. "Faster response of NO2 sensing in graphene–WO3 nanocomposites." *Nanotechnology* 23.20 (2012): 205501.

[23]Kaur, Jasmeet, et al. "Sensitive and selective acetone sensor based on Gd doped WO3/reduced graphene oxide nanocomposite." *Sensors and Actuators B: Chemical* 258 (2018): 1022-1035.

[24]Veeramani, Vediyappan, et al. "Heteroatom-enriched porous carbon/nickel oxide nanocomposites as enzyme-free highly sensitive sensors for detection of glucose." *Sensors and Actuators B: Chemical* 221 (2015): 1384-1390.

[25]Zilli, D., Pablo Ricardo Bonelli, and Ana Lea Cukierman. "Room temperature hydrogen gas sensor nanocomposite based on Pd-decorated multi-walled carbon nanotubes thin films." *Sensors and Actuators B: Chemical* 157.1 (2011): 169-176.

[26]Sayago, I., et al. "New sensitive layers for surface acoustic wave gas sensors based on polymer and carbon nanotube composites." *Sensors and Actuators B: Chemical* 175 (2012): 67-72.

[27]Van Hieu, Nguyen, et al. "Thin film polypyrrole/SWCNTs nanocomposites-based NH3 sensor operated at room temperature." *Sensors and Actuators B: Chemical* 140.2 (2009): 500-507.

[28]Serban, BogdanCatalin, et al. "Matrix nanocomposite containing aminocarbon nanotubes for carbon dioxide sensor detection." U.S. Patent No. 7,913,541. 29 Mar. 2011.

[29]Liu, Chengbin, et al. "Direct electrodeposition of graphene enabling the one-step synthesis of graphene–metal nanocomposite films." *small* 7.9 (2011): 1203-1206.

[30]Zarrin, Hadis, et al. "Functionalized graphene oxide nanocomposite membrane for low humidity and high temperature proton exchange membrane fuel cells." *The Journal of Physical Chemistry C* 115.42 (2011): 20774-20781.

[31]Wang, Yizhong, Minking K. Chyu, and Qing-Ming Wang. "Passive wireless surface acoustic wave CO2 sensor with carbon nanotube nanocomposite as an interface layer." *Sensors and Actuators A: Physical* 220 (2014): 34-44.

[32]Baibarac, Mihaela, and Pedro Gómez-Romero. "Nanocomposites based on conducting polymers and carbon nanotubes: from fancy materials to functional applications." *Journal of nanoscience and nanotechnology* 6.2 (2006): 289-302.

[33]Mun, Seongcheol, Yi Chen, and Jaehwan Kim. "Cellulose–titanium dioxide–multiwalled carbon nanotube hybrid nanocomposite and its ammonia gas sensing properties at room temperature." *Sensors and Actuators B: Chemical* 171 (2012): 1186-1191.

[34]Aroutiounian, V. M., et al. "Study of the surface-ruthenated SnO2/MWCNTs nanocomposite thick-film gas sensors." *Sensors and Actuators B: Chemical* 177 (2013): 308-315.

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